

Seawater pH and Atmospheric Carbon Dioxide

Pearson and Palmer (1) concluded that even though middle Eocene (43 Ma) global mean temperature was perhaps 5°C warmer than today, “atmospheric $p\text{CO}_2$ was probably similar to modern concentrations or slightly higher.” They suggest “either that Earth’s climate is very sensitive to small changes in $p\text{CO}_2$, or that the global cooling since the Eocene was not driven primarily by changes in $p\text{CO}_2$” This result has led some (2) to suggest that “the whole carbon dioxide paradigm is crumbling.”

Pearson and Palmer used boron isotopes to infer paleo-ocean pH, and then used this paleo-pH proxy to estimate paleo-atmospheric $p\text{CO}_2$ under the assumption of constant concentration of total dissolved inorganic carbon in seawater. However, carbon is continuously supplied to the atmosphere and ocean by degassing from metamorphism and magmatism and by the weathering of carbonate minerals and organic carbon, and is continuously consumed by the production of carbonate and organic carbon sediments (3). Hence, the total dissolved inorganic carbon load of the ocean could be expected to vary over time.

The carbonate chemistry of seawater is largely controlled by the twin constraints of atmospheric $p\text{CO}_2$ and ocean carbonate-ion concentration (3). The mean partial pressure of CO_2 in the surface ocean is nearly equal to that of the atmosphere. Because the ocean is in contact with carbonate sediments, both on shelves and in the deep sea, the ocean as a first approximation is roughly saturated with respect to calcite. If we assume that the concentration of Ca^{2+} has remained nearly constant, this is equivalent to a roughly constant

carbonate-ion concentration (CO_3^{2-}).

Under this assumption we can predict $p\text{CO}_2$ as a function of the hydrogen-ion concentration, or pH, using:

$$p\text{CO}_2 = K_H[\text{H}^+]^2 [\text{CO}_3^{2-}]/K_1K_2, \quad (1)$$

where K_H is the Henry’s law constant for CO_2 , and K_1 and K_2 are the first and second dissociation constants for carbonic acid. Equation 1 scales with the square of the hydrogen-ion concentration, whereas the equation used by Pearson and Palmer roughly scales directly with the hydrogen-ion concentration (Fig. 1). Hence, the assumption of constant carbonate-ion concentration yields far greater pH sensitivity than does the assumption of constant total dissolved inorganic carbon concentration.

If we assume that the preindustrial surface ocean had a pH of 8.25, Eq. 1 yields a $p\text{CO}_2$ of ~2.5 times the preindustrial atmospheric value for the pH of 8.05 inferred by Pearson and Palmer for the Eocene surface ocean. If climate sensitivity to enhanced atmospheric CO_2 is 1.5° to 4.5°C per CO_2 -doubling (4), then this yields 2° to 6°C CO_2 -induced warming for the Eocene, which suggests that enhanced atmospheric CO_2 content could explain much or all of inferred Eocene warmth. In this calculation we have assumed that the carbonate ion concentration is constant, and therefore a large variation in calcium carbonate saturation state in the surface ocean is not implied. However, the Eocene ocean overall was probably more acidic than at present, as suggested by a distinctly shallower carbonate compensation depth at that time (5), and this in itself suggests that the Eocene atmospheric CO_2 level was higher than it is today. Factors

such as biological productivity could affect the surface-ocean carbonate ion concentration and thereby affect the predicted $p\text{CO}_2$ in the surface ocean. Nevertheless, we have shown here that pH values inferred by Pearson and Palmer are entirely consistent with large amounts of CO_2 in the Eocene atmosphere. Therefore, reports of the death of the carbon dioxide paradigm are exaggerated.

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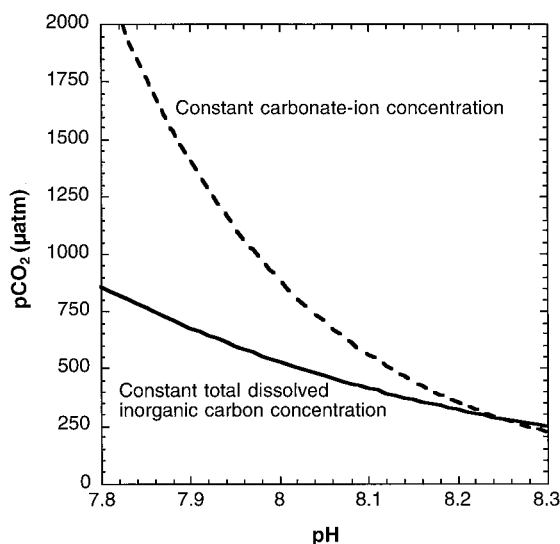
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Pearson and Palmer (1) use boron isotope measurements to infer sea surface pH values for the middle Eocene. From these values they argue that the carbon dioxide concentration in the mid-Eocene atmosphere was similar to modern values. However, their calculation of equilibrium atmospheric $p\text{CO}_2$ from sea surface pH is based on the invalid assumption of a modern oceanic total CO_2 (ΣCO_2) concentration for the middle Eocene. They conclude that a higher ΣCO_2 value “is unreasonable because it would imply a larger variation in calcium carbonate saturation in the oceans than is compatible with the geologic record.” Figure 1 [of (2)] shows that a wide range of calcite saturation states can occur at virtually any ΣCO_2 concentration, as long as changes in ΣCO_2 are accompanied by corresponding changes in total alkalinity (A_T). Such changes are not at all unreasonable; they are implicit in any scenario for changes in atmospheric CO_2 levels due to long-term shifts in the carbonate-silicate geochemical cycle (3–5). Changes in oceanic ΣCO_2 have long been known as a prerequisite for the occurrence of large changes in atmospheric CO_2 in the geologic past (2, 6).

Figure 1 also shows that a wide range of equilibrium $p\text{CO}_2$ values can be calculated for surface waters associated with any given calcite saturation condition in the deep ocean.

Fig. 1. Partial pressure of CO_2 in the atmosphere ($p\text{CO}_2$) as a function of pH computed assuming (solid line) a constant total dissolved inorganic carbon concentration, and (dashed line) a constant carbonate-ion concentration, in the surface ocean. Both curves assume a pH of 8.25 at 280 ppm. The pH range 7.91 to 8.33 estimated by (7) is consistent with CO_2 -induced warming in the middle Eocene.



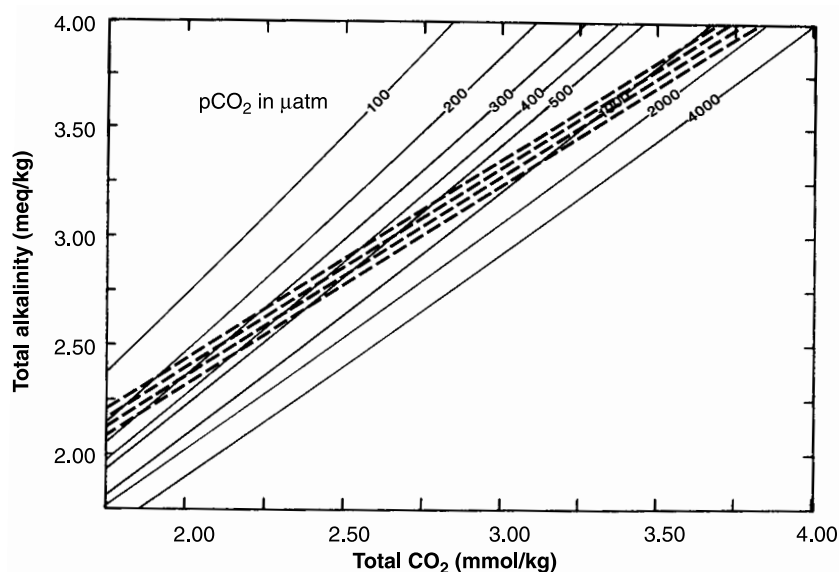


Fig. 1. Warm surface water A_T and ΣCO_2 values corresponding to calcite saturation horizon depths (dotted lines) and atmospheric CO_2 partial pressures (solid lines) (2). Saturation horizon contours (from top to bottom, 5000, 4000, 3000, and 2000 m) were calculated for deep water compositions derived from the surface water values shown by adding appropriate mean differences ($\Delta A_T = 80 \times 10^{-6}$ eq/kg; $\Delta \Sigma\text{CO}_2 = 300 \times 10^{-6}$ mol/kg). The calculation assumed a deep ocean salinity of 34.7‰ and temperatures of 2.5°C at 2000 m, 2.0°C at 3000 m, 1.5°C at 4000 m, and 1.0°C at 5000 m. The pCO_2 contours were calculated for the warm surface water values shown, assuming a salinity of 35.2‰ and a temperature of 22°C. Further details of the calculations are given in (2).

Pearson and Palmer's best estimate of 8.05 for mid-Eocene surface pH, combined with the shallower calcite compensation depth of the middle Eocene (7), can be shown to imply deep ocean ΣCO_2 and A_T values that are at least 50 percent higher than modern values. This scenario would be consistent with an equilibrium atmospheric pCO_2 three to four times the preindustrial value. These calculations would vary somewhat for different assumed temperatures and salinities, but the general features of Fig. 1 would remain the same.

Estimates of past sea surface pH are a very valuable addition to the information needed to understand the geologic history of atmospheric CO_2 . However, these estimates must be supplemented by careful consideration of other constraints and by testing of hypothesized changes in past oceanic chemistry.

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Response: Sundquist, and Caldeira and Berner make the important point that our best estimate of middle Eocene atmospheric pCO_2 (370 to 400 ppm) may be low because we assumed a value for total dissolved inorganic carbon (ΣCO_2) that is equal to that today. If ΣCO_2 was higher, then our estimate of pCO_2 would need to be revised upward.

In our report we were clear that in order to calculate pCO_2 , some value of ΣCO_2 must be taken. Because the actual level of ΣCO_2 at 43 million years ago is not well known, we provided a diagram [figure 3 in (1)] that allowed the reader to estimate pCO_2 for ΣCO_2 values up to 250% of the modern. Readers are invited to substitute whatever value they think is most appropriate. The diagram is similar in its essentials to figure 1 of Sundquist.

The great promise of the boron isotope

technique is that it will soon be possible to analyze large numbers of samples with excellent stratigraphic resolution, as is currently the case, for example, with oxygen isotopes. It is likely that pCO_2 , ΣCO_2 , and the carbonate compensation depth fluctuated considerably in the Eocene, possibly even on Milankovitch time scales ($<100,000$ years). General statements about enhanced metamorphic and magmatic outgassing rates in the Eocene as a whole may not be relevant to the situation in a specific narrow time window in the middle Eocene (43 Ma). Thus, while it may be the case that ΣCO_2 was 50 percent higher, as Sundquist believes, we do not feel confident enough about the evidence from generalized geological considerations to rely on this assumption.

Caldeira and Berner make the interesting suggestion that a good assumption to make in order to calculate pCO_2 from surface ocean pH might be that the total carbonate ion concentration in the surface ocean was the same as that today. A potential advantage of this is that pCO_2 can be estimated with greater sensitivity than if we assume constant ΣCO_2 . However, as Caldeira and Berner make clear, the approach relies on the assumption that the calcium ion (Ca^{2+}) concentration of the ocean has not changed, which may not be the case. We know of no reliable geochemical proxy for Ca^{2+} in the surface ocean. Modeling studies [see figure 9 in (2)] suggest that Ca^{2+} concentration may have changed by a factor of 3 in the Cenozoic. Thus, while the suggestion of Caldeira and Berner may prove valuable, more work needs to be done on proxies for Ca^{2+} .

These comments underline the need for the development of quantitative determinations of past ΣCO_2 variation so that pCO_2 estimates using the boron isotope technique can be made more accurate.

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